Experimental Verification by Idaho National Engineering Laboratory

Methods

A search for excess heat during the electrolysis of aqueous potassium carbonate (K^+/K^+ electrocatalytic couple) was investigated using cells supplied by HydroCatalysis Power Corporation and a cell fabricated by Idaho National Engineering Laboratory (INEL). To simplify the calibration of these cells, they were constructed to have primarily conductive and forced convective heat losses. Thus, a linear calibration curve was obtained. Differential calorimetry was used to determine the cell constant which was used to calculate the excess enthalpy. The cell constant was calculated during the experiment (on-the-fly-calibration) by turning an internal resistance heater off and on, and inferring the cell constant from the difference between the losses with and without the heater.

The general form of the energy balance equation for the cell in steady state is:

$$0 = P_{appl} + Q_{htr} + Q_{xs} - P_{gas} - Q_{loss} \qquad (III.1)$$

where P_{appl} is the electrolysis power; Q_{htr} is the power input to the heater; Q_{xs} is the excess heat power generated by the hydrogen "shrinkage" process; P_{gas} is the power removed as a result of evolution of H_2 and O_2 gases; and Q_{loss} is the thermal power loss from the cell. When an aqueous solution is electrolyzed to liberate hydrogen and oxygen gasses, the electrolysis power P_{appl} ($=E_{appl}I$) can be partitioned into two terms:

$$P_{appl} = E_{appl}I = P_{cell} + P_{gas} \qquad (III.2)$$

An expression for P_{gas} ($=E_{gas}I$) is readily obtained from the known enthalpy of formation of water from its elements:

$$E_{gas} = \frac{-\Delta H_{form}}{\alpha F} \qquad (III.3)$$

(F is Faraday's constant), which
yields $E_{gas} = 1.48$ V for the reaction

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2 \qquad (III.4)$$

The net faradaic efficiency of gas evolution is assumed to be unity; thus, Eq. (III.2) becomes

$$P_{cell} = (E_{appl} - 1.48V)I \qquad (III.5)$$

The cell was calibrated for heat losses by turning an internal resistance heater off and on while maintaining constant electrolysis and by inferring

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the cell constant from the difference between the losses with and without the heater where heat losses were primarily conductive and forced convective losses. When the heater was off, the losses were given by

$$c(T_C - T_b) = P_{appl} + 0 + Q_{xs} - P_{gas} \qquad (III.6)$$

where c is the heat loss coefficient; T_b is ambient temperature and T_C is the cell temperature. When a new steady state is established with the heater on, the losses change to:

$$c(T_C' - T_b) = P'_{appl} + Q_{htr} + Q'_{xs} - P'_{gas} \qquad (III.7)$$

where a prime superscript indicates a changed value when the heater was on. When the following assumptions apply

$$Q_{xs} = Q'_{xs}; P_{appl} = P'_{appl}; P_{gas} = P'_{gas} \qquad (III.8)$$

the cell constant or heating coefficient a, the reciprocal of the heat loss coefficient(c), is given by the result

$$a = \frac{T_C' - T_C}{Q_{htr}} \qquad (III.9)$$

In all heater power calculations, the following equation was used

$$Q_{htr} = E_{htr}I_{htr} \qquad (III.10)$$

LIGHT WATER CALORIMETRY EXPERIMENTS

INEL EXPERIMENT I (DC Operation)

The present experiments were carried out by observing and comparing the temperature difference, $\Delta T_1 = T(\text{electrolysis only}) - T(\text{blank})$ and $\Delta T_2 = T(\text{electrolysis plus resistor heating}) - T(\text{blank})$ referred to unit input power.

The cell comprised a 10 gallon (33 in. x 15 in.) Nalgene tank (Model # 54100-0010). Two 4 inch long by 1/2 inch diameter terminal bolts were secured in the lid, and a cord for a heater was inserted through the lid.

The cathode comprised 1.) a 5 gallon polyethylene bucket which served as a perforated (mesh) support structure where 0.5 inch holes were drilled over all surfaces at 0.75 inch spacings of the hole centers and 2.) 5000 meters of 0.5 mm diameter clean, cold drawn nickel wire (NI 200 0.0197", HTN36N0AG1, A1 Wire Tech, Inc.). The wire was wound uniformly around the outside of the mesh support as 150 sections of 33 meter length. The ends of each of the 150 sections were spun to form three cables of 50 sections per cable. The cables were pressed in a terminal connector which was bolted to the cathode terminal post. The connection was covered with epoxy to prevent corrosion.

The anode comprised an array of 15 platinized titanium anodes (15 - Engelhard Pt/Ti mesh 1.6" x 8" with one 3/4" by 7" stem attached to the 1.6" side plated with 100 U series 3000). A 3/4" wide tab was made at the end of the stem of each anode by bending it at a right angle to the anode. A 1/4" hole was drilled in the center of each tab. The tabs were bolted to a 12.25" diameter polyethylene disk (Rubbermaid Model #2666) equidistantly around the circumference. Thus, an array was fabricated having the 15 anodes suspended from the disk. The anodes were bolted with 1/4" polyethylene bolts. Sandwiched between each anode tab and the disk was a flattened nickel cylinder also bolted to the tab and the disk. The cylinder was made from a 7.5 cm by 9 cm long x 0.125 mm thick nickel foil. The cylinder traversed the disk and the other end of each was pressed about a 10 A /600 V copper wire. The connection was sealed with

Teflon tubing and epoxy. The wires were pressed into two terminal connectors and bolted to the anode terminal. The connection was covered with epoxy to prevent corrosion.

Before assembly, the anode array was cleaned in 3 M HCl for 5 minutes and rinsed with distilled water. The cathode was cleaned in 3% H_2O_2/ 0.57 M K_2CO_3 and rinsed with distilled water. The anode was placed in the cathode support and the electrode assembly was placed in the tank containing electrolyte. The power supply was connected to the terminals with large cables.

The electrolyte solution comprised 28 liters of 0.57 M K_2CO_3 (Alfa K_2CO_3 99%) in the case of the MC 3 cell or 28 liters of 0.57 M Na_2CO_3 (Alfa Na_2CO_3 99%) in the case of the MC 2 cell.

The heater comprised a 57 ohm 1500 watt Incoloy coated cartridge heater which was suspended from the polyethylene disk of the anode array. It was powered by a regulated power supply. The voltage was measured with a digital meter, and the current was measured as a voltage across a precision resistor with a digital meter.

The stirrer comprised a 1 cm diameter by 43 cm long glass rod to which an 8 cm by 2.5 cm Teflon half moon paddle was fastened at one end. The rod passed through a bearing hole in the tank lid and through a bearing hole in the center of the anode array disk. The other end of the stirrer rod was connected to a variable speed stirring motor. The stirrer shaft was rotated at 4 Hz. With the stirrer connected, the stirrer motor drew 4.7 W. With the stirrer disconnected, the stirrer drew 4.4 W; thus, 0.3 W was the stirrer power.

Electrolysis was performed at 39.5 amps constant current with a constant current power supply. The cells were operated in the environmental chamber in the INEL Battery test Laboratory. The chamber maintained the average temperature of the cell surroundings within 1 ^0C. The bottom of the cell rested on a 1/2 inch thick sheet of Styrofoam.

The temperature was recorded with a series of Teflon-coated Type E thermocouples inserted in several places. The ambient temperature reference was a closed one-liter container of water

with a thermocouple nominally in the center of the water volume.

Data from thermocouples, voltages, and currents were logged by one of the Battery Lab's computer based data systems and recorded at 5 minute intervals. The delta temperature ($\Delta T = T$(electrolysis only) – T(blank)) and electrolysis power were plotted. The heating coefficient was determined "on the fly" by the addition of heater power. The delta temperature $\Delta T_2 = T$(electrolysis + heater) – T(blank)) and the electrolysis power and heater power were plotted.

Mass spectroscopy of the gasses evolving from the MC 3 (K_2CO_3) cell was performed using a VG Instruments model SXP-50 high -precision mass spectrometer with 0.01-amu mass resolution and 6 decade sensitivity.

A 100 ml sample of the 0.57 M K_2CO_3 electrolyte of the MC 3 (K_2CO_3) cell was removed after 20 days of cell operation, and a chemical analysis was performed on the electrolyte using an Inductively Coupled Plasma-Atomic Emission Spectrometer.

RESULTS

Light Water Calorimetry

The results of the electrolysis for INEL cell runs MC 2 and MC 3 at 39.5 A constant current appear in Figure 1 (hand plot of data by INEL scientists). As shown in Figure 1, the MC 3 (K_2CO_3) cell intercepts the Total Input Power axis at 35 W; whereas, the MC 2 (Na_2CO_3) cell intercepts the Total Input Power axis at 59 W. The input power to electrolysis gases given by Eqs. (III.2-III.5) is (39.5)(1.48) = 58.5 W. The production of excess enthalpy of 25 W is observed with the MC 3 (K_2CO_3) cell, and energy balance is observed with the MC 2 (Na_2CO_3) cell.

Mass spectroscopic analysis of the gasses evolved by the MC 3 (K_2CO_3) cell showed that a significant fraction of the sample was air with standard constituents. When the spectrum associated with air was removed, the residue showed a majority of diatomic hydrogen and oxygen gases in approximately the 2:1 proportion expected from the electrolysis and residual water vapor. There were no hydrocarbons, no metallic constituents or other anomalies except that a slightly higher than expected hydrogen to oxygen ratio was observed. No

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tritium or deuterium measurements above normal background were observed.

Chemical analysis of an electrolyte sample from the MC 3 (K_2CO_3) cell after 20 days of operation found the following components at levels above the background levels in the water used to fill and replenish the cell: 1.7 ppm silicon, 1.1 ppm sulfur, and 46.5 ppm sodium in addition to the K_2CO_3 salt. Small quantities of silicon are known impurities in the nickel wire and may have also come from the glassware used in various processes. Sulfur is a common impurity in the salt, and it may have come from the resin beds used for water deionization. Sodium is a probable salt impurity, and it may also have come from hand contact with the system. The potassium was measured at 43,000 µg/ml corresponding to a salt molarity of 0.55 M (within measurement error of the initial 0.57 molarity determined by weighing the salt and measuring the water for the initial charge). The electrolyte retained its molarity. The cell potential characteristics were essentially unchanged over the duration of operation. There were no nickel or other metallic compounds present in the electrolyte. A visual inspection of the cell showed that all of the structural components were intact. The cell comprised about 155 moles of nickel in the cathode, about 6.5 moles of titanium in the anodes, and about 13.7 moles of K_2CO_3. The only material consumed in the cell was nano-pure deionized water.

INEL EXPERIMENT II (Pulsed Power Operation)

The MC 3 (K_2CO_3) cell was wrapped in a one-inch layer of urethane foam insulation about the cylindrical surface. The top was not insulated. The bottom of the cell rested on a 1/2 inch thick sheet of Styrofoam.

The cell was operated in a pulsed power mode. A current of 10 amperes was passed through the cell for 0.2 seconds followed by 0.8 seconds of zero current for the current cycle. The cell voltage was about 2.4 volts, for an average input power of 4.8 W. The electrolysis power average (Eq. (III.5)) was 1.84 W, and the stirrer power was measured to be 0.3 W. Thus, the total average net input power was 2.14 W. The cell was operated at various resistance heater settings, and the temperature

difference between the cell and the ambient as well as the heater power were measured.

RESULTS
Light Water Calorimetry

The results of the excess power as a function of cell temperature with the MC 3 cell operating in the pulsed power mode at 1 Hz with a cell voltage of 2.4 volts, a peak current of 10 amperes, and a duty cycle of 20 % appears in Figure 2.

Figure 2 shows that the excess power is temperature dependent for pulsed power operation, and the maximum excess power shown in Figure 2 is 18 W for an input electrolysis joule heating power of 2.14 W. Thus, the ratio of excess power to input electrolysis joule heating power is 850 %.

INEL EXPERIMENT III (Forced Convection Calorimetry Of INEL Cell)

INEL scientists constructed an electrolytic cell comprising a nickel cathode, a platinized titanium anode, and a 0.57 M K_2CO_3 electrolyte. The cell design appears in Appendix 1. The cell was operated in the environmental chamber in the INEL Battery test Laboratory at constant current, and the heat was removed by forced air convection in two cases. In the first case, the air was circulated by the environmental chamber circulatory system alone. In the second case, an additional forced air fan was directed onto the cell.

The cell was equipped with a water condensor, and the water addition to the cell due to electrolysis losses was measured.

RESULTS
Light Water Calorimetry

The data of the forced convection heat loss calorimetry experiments during the electrolysis of a 0.57 M K_2CO_3 electrolyte with the cell appears in Table 1 and Figure 3. The comparison of the calculated and measure water balance of the INEL cell appears in Table 2 and Figure 4.

The intercept of the Net Input Power (calculated using Eq. (III.5)) axis of Figure 3 for both cases of forced convection is 13 W. Thus, 13 W of excess power was produced by the INEL cell. This excess power can not be attributed to recombination of the hydrogen and oxygen as indicated by the

equivalence of the calculated and measured water balance as shown in Figure 4.

THERMAL CONDUCTANCE CALIBRATION (11/25)

Figure 1.

Tc-Ta

40.00
35.00
30.00
25.00
20.00
15.00
10.00
5.00
0.00

0.00   50.00   100.00   150.00   200.00   250.00   300.00

Total Input Power (W)
(Electrolysis not deducted)

Figure 2.

$y = 7.4567 + 0.40500x \quad R^2 = 1.000$
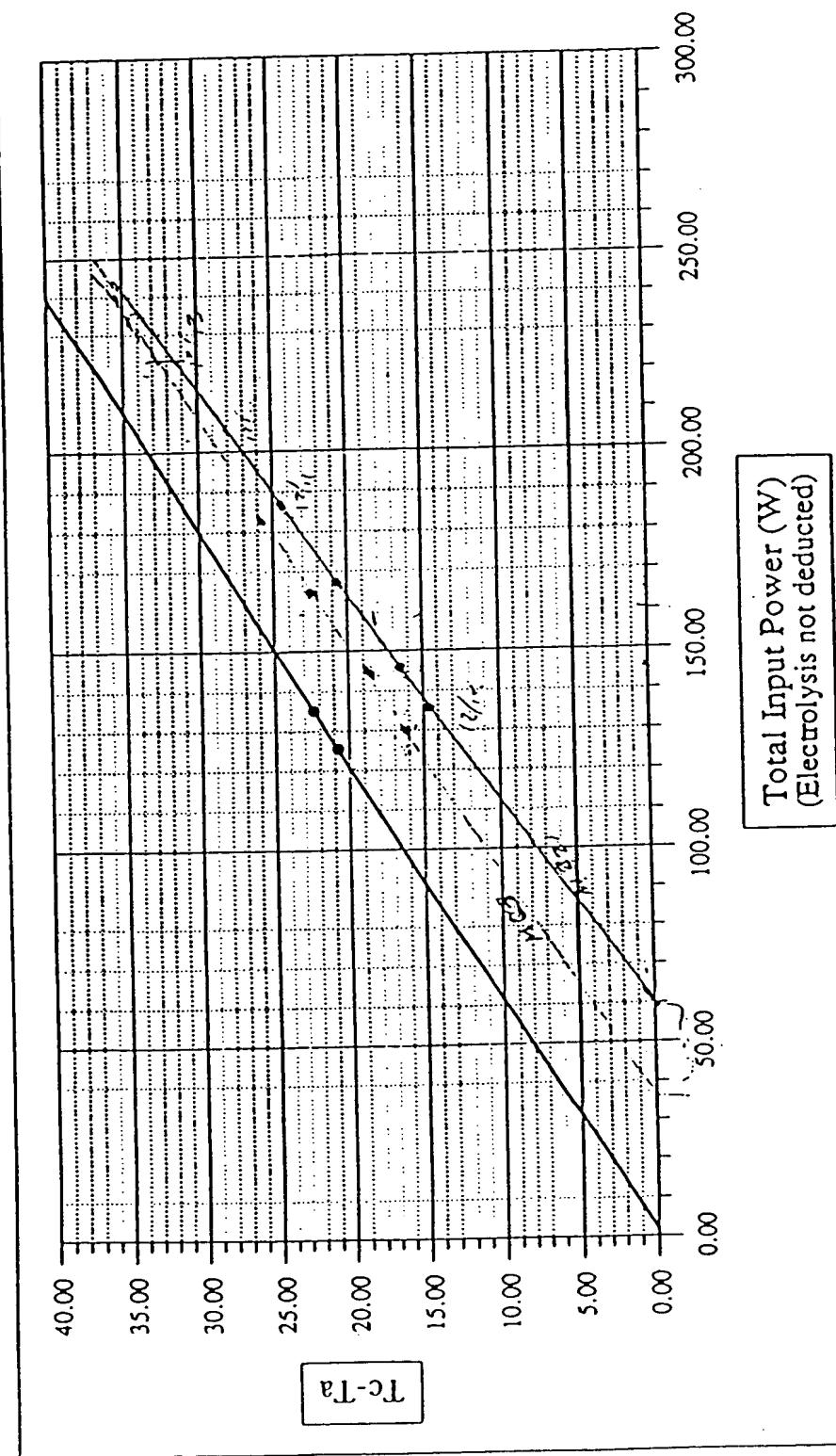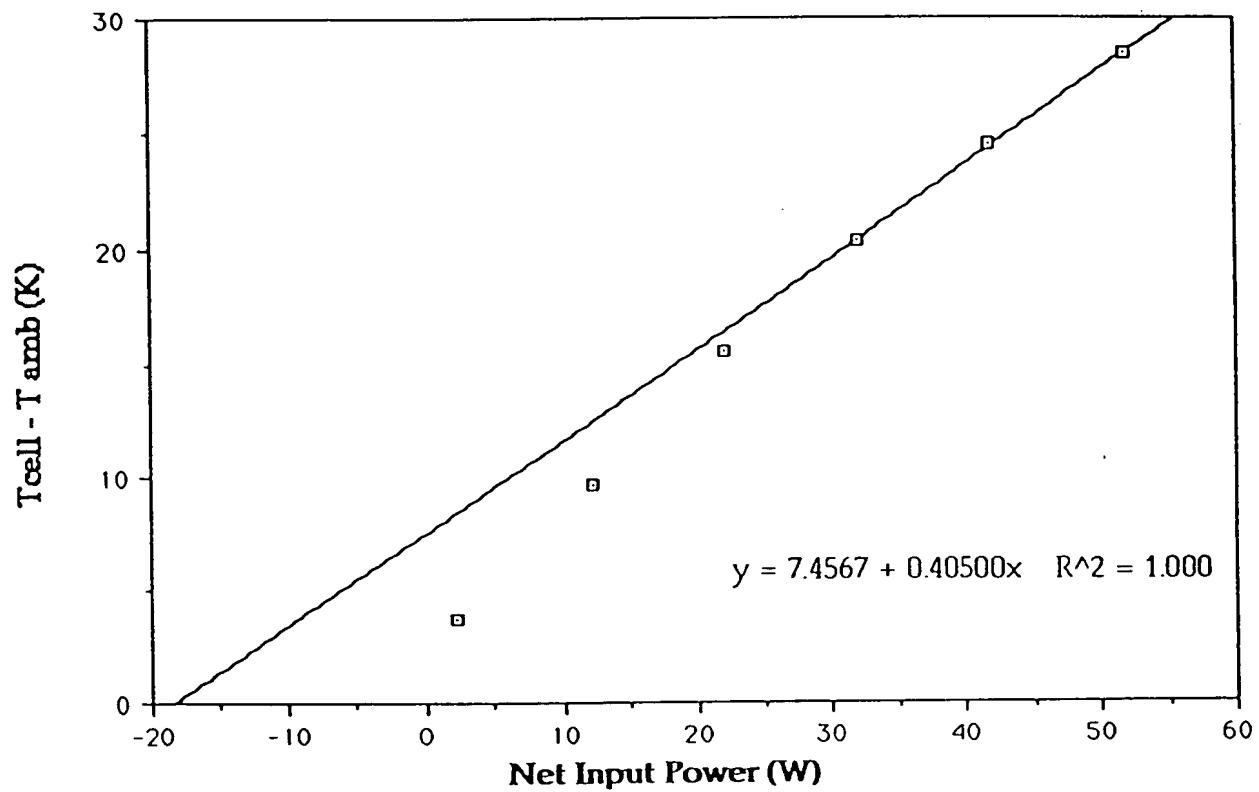
Figure 3.

IC1

T99 THRU T103 & T105 THRU T109

DELTA TEMPERATURE [Tcell-Tamb] (DEG.C)

NET INPUT POWER (WATTS)

[TOTAL POWER - 1.48*ELECTRODE CURRENT]

WITHOUT FAN
DATA & LINEAR FIT

WITH FAN
DATA & LINEAR FIT
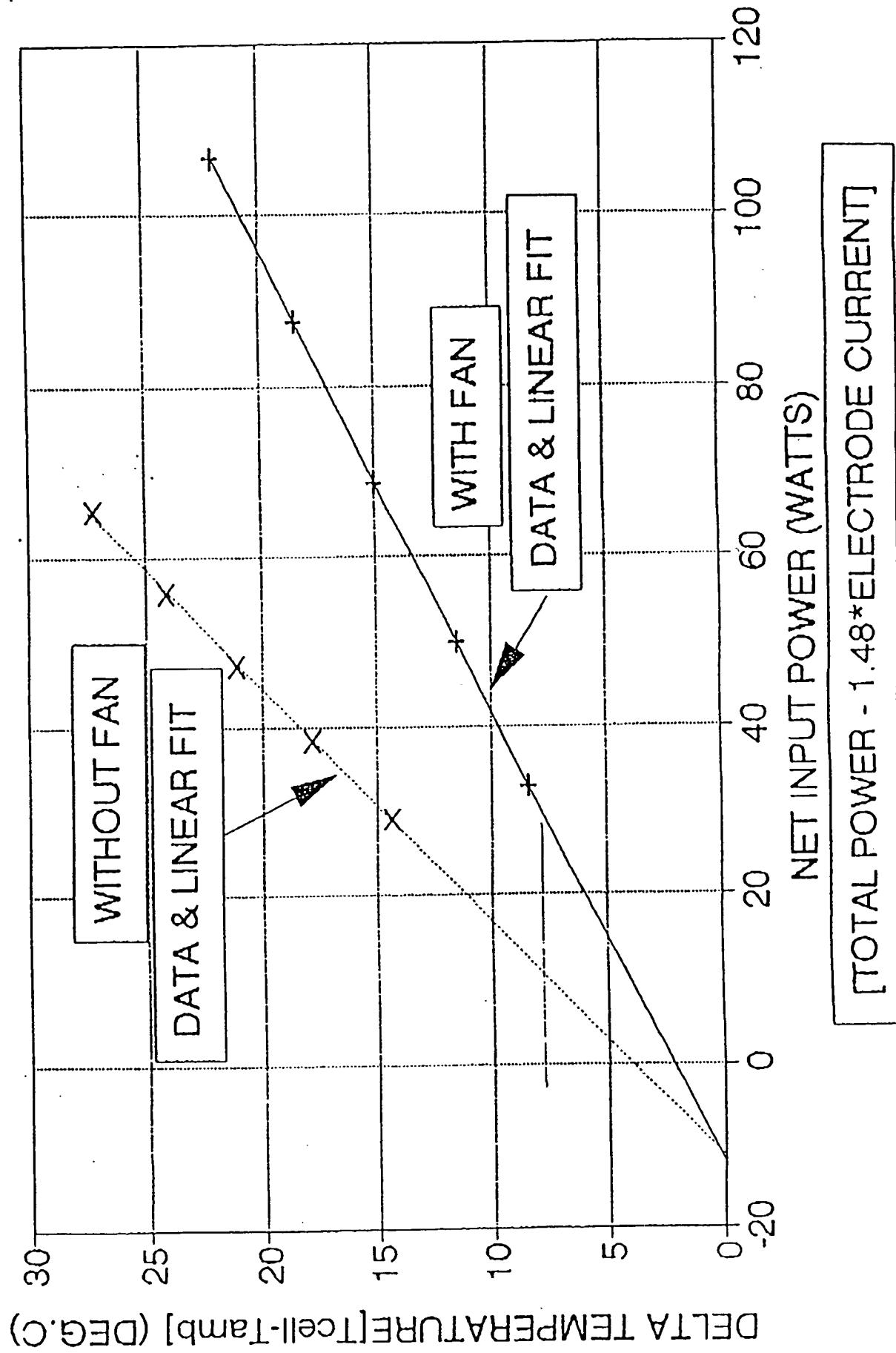
IC1 WATER ADDITION
1/9/93 THRU 1/29/93

TOTAL WATER ADDED (GRAMS)

TIME (DAYS)

MEASURED

CALCULATED
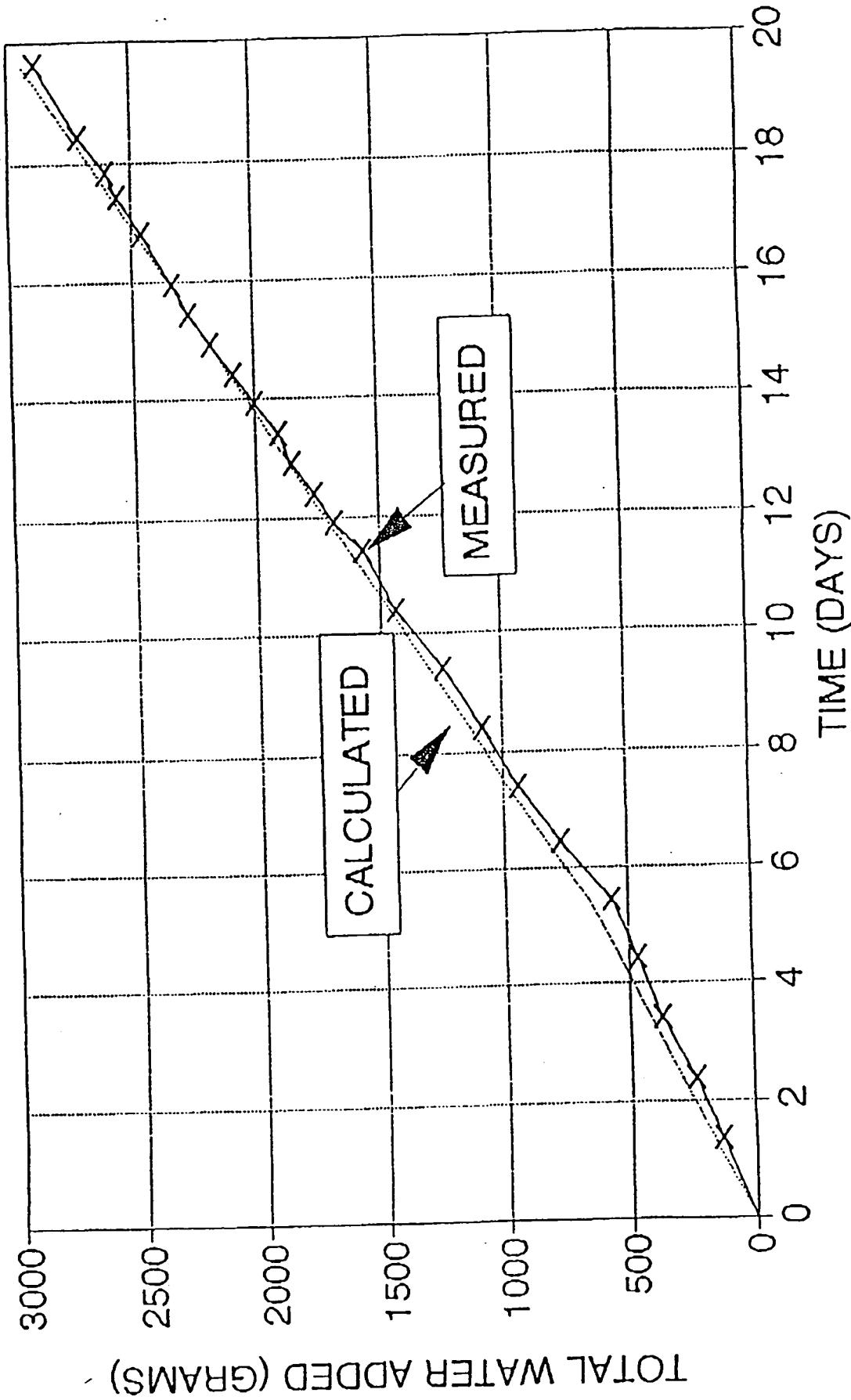
Table 1.

FILE IC1

TEST NO.	TOTAL POWER	DELTA TEMP	LF DT	DELTA TEMP	LF DT	PWR-A*1.48
T99	94.8	27.2	27.36265			65.2962
T100	85.2	24.05	23.93155			55.6962
T101	76.8	21.05	20.92933			47.2962
T102	67.8	17.75	17.71267			38.2962
T103	58.57	14.3	14.4138			29.0662
	18.24		-0.00042			-11.2638
T105	136.07			21.95	21.94573	106.6662
T106	117.05			18.42	18.42674	87.5462
T107	98.25			14.95	14.94844	68.7462
T108	79.45			11.47	11.47015	49.9462
T109	62.68			8.35	8.348937	33.0762
	17.45				-0.00082	-12.0538

Table 2.

ICI WATER ADDITION ;FILE ICIWATER

DATE	TIME HOURS	MINUTES	SECONDS	QPRO TIME	QPRO DATE+TIM	DATE-START DAYS	ELEOTRO AMPS	WATER GRAMS	WATER TOTAL	WATER CALC	TOTAL CALC	ADDED/CALC
								0	0	0	0	0
01/09/93	21	30	0	0.895833	33978.9	-0.00416667	16	0	0	169.9935	169.9935	0.77061781
01/11/93	7	15	0	0.302083	33980.3	1.402083333	15	131	131	120.4645	290.468	0.82983844
01/12/93	7	10	0	0.298611	33981.3	2.398611111	15	108	239	121.9893	412.4473	0.89708429
01/13/93	7	29	0	0.311806	33982.31	3.411805556	14.94	131	370	122.6582	535.1056	0.8577747
01/14/93	7	56	0	0.330556	33983.33	4.430555556	14.94	89	459	119.8188	654.9243	0.8566875
01/15/93	7	50	0	0.326389	33984.33	5.426388889	14.93	102	561	164.6302	819.5548	0.93485404
01/16/93	8	26	0	0.351389	33985.35	6.461388889	19.93	205	766	160.8341	979.3887	0.9536691
01/17/93	8	19	0	0.346528	33986.36	7.446527778	19.93	168	934	158.5665	1135.955	0.95420301
01/18/93	7	42	0	0.320833	33987.32	8.420833333	19.94	160	1094	159.4995	1295.455	0.95854903
01/19/93	7	32	0	0.313889	33988.31	9.413888889	19.93	164	1238	159.9143	1455.369	0.98394292
01/20/93	7	25	0	0.309028	33989.31	10.40902778	19.94	194	1432	162.511	1617.88	0.98731626
01/21/93	7	42	0	0.320833	33990.32	11.42083333	19.93	133	1565	78.7489	1696.626	0.95754809
01/21/93	10	28	0	0.611111	33990.61	11.91111111	19.93	110.5	1675.5	80.76359	1777.379	0.98937791
01/22/93	7	32	0	0.313889	33991.31	12.41388889	19.93	83	1758.5	80.66513	1858.245	0.9958323
01/22/93	19	37	0	0.817361	33991.82	12.91736111	19.93	92	1850.5	79.76976	1938.034	0.97856882
01/23/93	7	32	0	0.313889	33992.31	13.41388889	19.94	48	1898.5	78.86744	2016.892	0.99088111
01/23/93	19	19	0	0.804861	33992.8	13.90486111	19.93	102	2000.5	81.31128	2098.203	0.99261693
01/24/93	7	28	0	0.311111	33993.31	14.41111111	19.93	84	2082.5	79.41813	2177.618	0.99902727
01/24/93	19	20	0	0.805556	33993.81	14.90555556	19.93	93	2175.5	82.31512	2259.933	1.00423316
01/25/93	7	38	0	0.318056	33994.32	15.41805556	19.93	94	2269.5	82.87261	2342.806	0.99846461
01/25/93	20	1	0	0.834028	33994.83	15.93402778	19.93	65	2334.5	137.1919	2479.998	0.99052498
01/26/93	16	31	0	0.688194	33995.69	16.76819444	19.93	122	2456.5	101.9468	2581.944	0.98859824
01/27/93	7	45	0	0.322917	33996.32	17.42291667	19.93	96	2552.5	85.8406	2647.784	0.98518331
01/27/93	17	35	0	0.732639	33996.73	17.83263889	19.94	55	2608.5	95.03047	2742.815	0.99004131
01/28/93	7	47	0	0.324306	33997.32	18.42430556	19.93	107	2715.5	194.5085	2937.323	0.98289741
01/29/93	12	50	0	0.634722	33998.53	19.63472222	19.94	171	2886.5			

Appendix I.

DATE: December 15, 1992

TO: Richard Deaton MS 4139, Ext. 6-2016, FAX 6-2681

FROM: R. L. Drexler MS 3123, Ext. 6-1789

SUBJECT: INEL CELL CATHODE ESTIMATE

Attached are the following sketches and revised sketches:

Cathode Assembly for INEL CELL	12/15/92
Narrow Cathode Strap for INEL CELL	12/15/92
Cathode C-1 INEL CELL	12/2/92
Mandrel - Cathode Winding	12/8/92
Electrode Bus Ring INEL CELL	12/15/92

Would you please give us a firm estimate for fabrication of two "identical" cathode assemblies per the 12/15/92 sketch, and two Electrode Bus Rings per the 12/15/92 sketch.

The cathode windings could be made on a mandrel per the sketch 12/8/92 or similar suitable arrangement.

These cathodes and bus rings are similar to those previously fabricated except:

1. The straps are 0.5 in. wide rather than 1.0 in. wide. These narrower straps would be flat rather than arched to fit the winding curvature.

2. There are no secondary straps as were added to the windings of the first cathode assembly.

3. Windings would be less dense than the first winding. A much steeper pitch is probably necessary to achieve the more open wind.

4. Weight of the NI-200 wire of each winding should be very close to 3.33 pounds, and both windings should have the same weight as closely as possible.

5. Slots in the Teflon Buss Ring for the cathode straps would be 0.50 wide rather than the 1.0 width of the first ring.

INEL CELL

INEL CELL

OFF-GAS

CONDENSER

COOLING WATER

ELECTROLYTE FILL TUBE

ELECTROLYTE LEVEL

CATHODE POWER

CATHODE

ANODE

TEFLON DISCS

TEFLON PLUG

PYREX LID

T/C LEADS

ANODE POWER

TEFLON RING

PYREX VESSEL

HEATER

STIR SPACE

0 1 2 3 4 5 6
INCHES
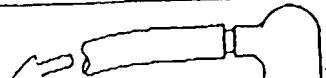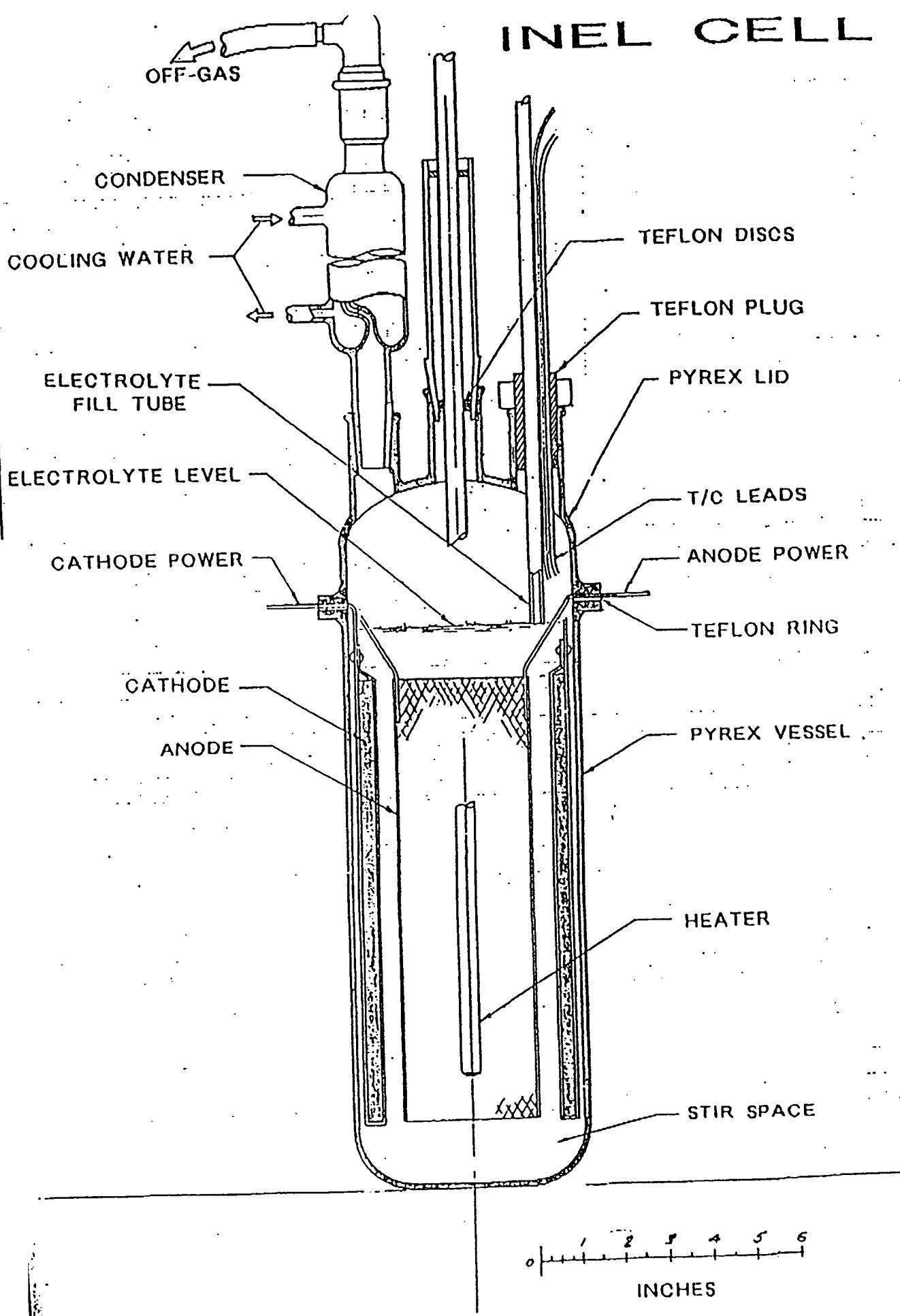
CATHODE ASSEMBLY

FOR
INEL CELL

CATHODE STRAP
2X

CATHODE WINDING

RIVET 6X - MAKE FROM
0.187 Ø NI-200 ROD.
INSTALL FOR TIGHT CLAMPING
LOAD BETWEEN STRAPS AND
WINDING.

5.125 MAX
OVER RIVETS

△ ALIGN BOTH STRAPS
IN PLANE AT 90°
WITH WINDING ₵

NARROW CATHODE STRAP

FOR
INEL CELL

12-15-92

0.13 × 45°
4X

0.25 ⌀

0.4

0.5

1.0

A

A

0.25 R

3.0

1.8

1.5

2.5

6.0

9.8

0.188 ⌀ THRU
BOTH SIDES
3X

11.8

0.19 R

SCALE - FULL
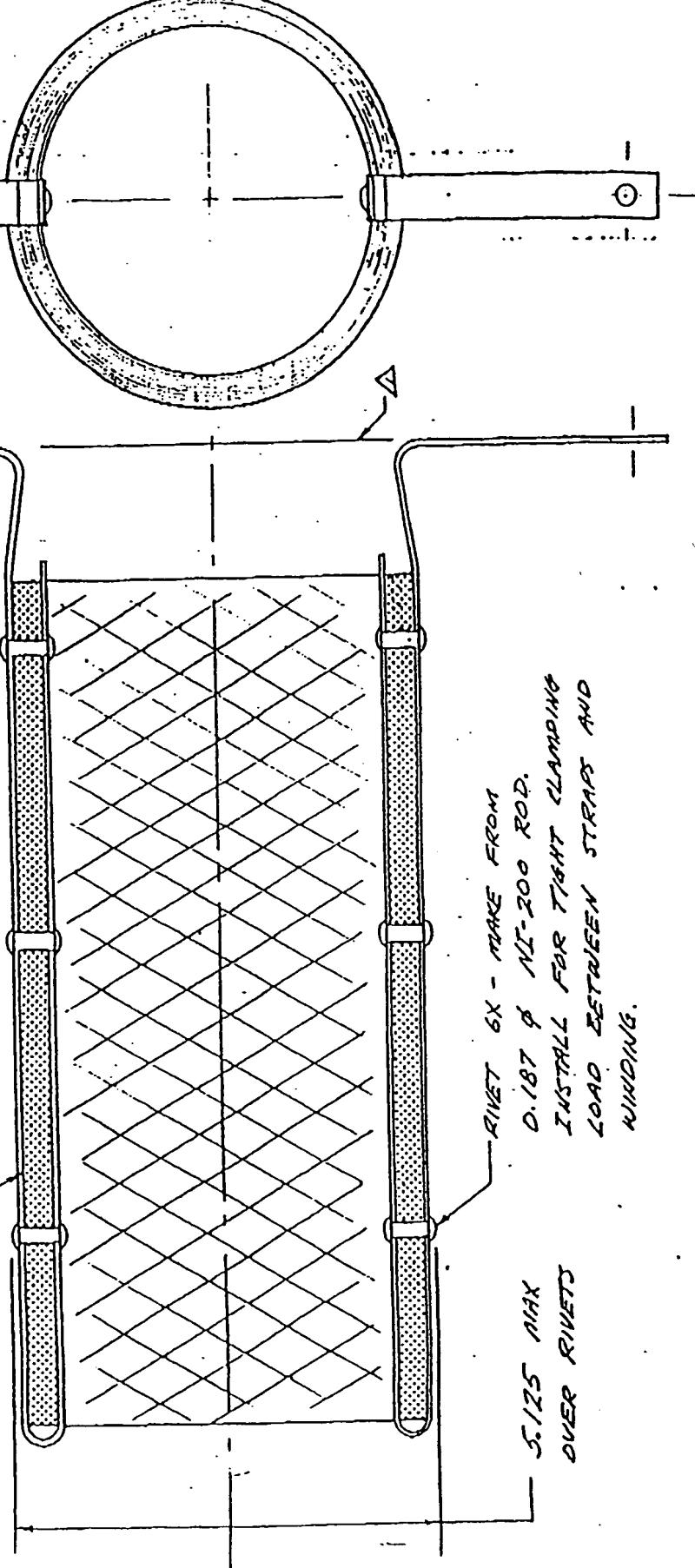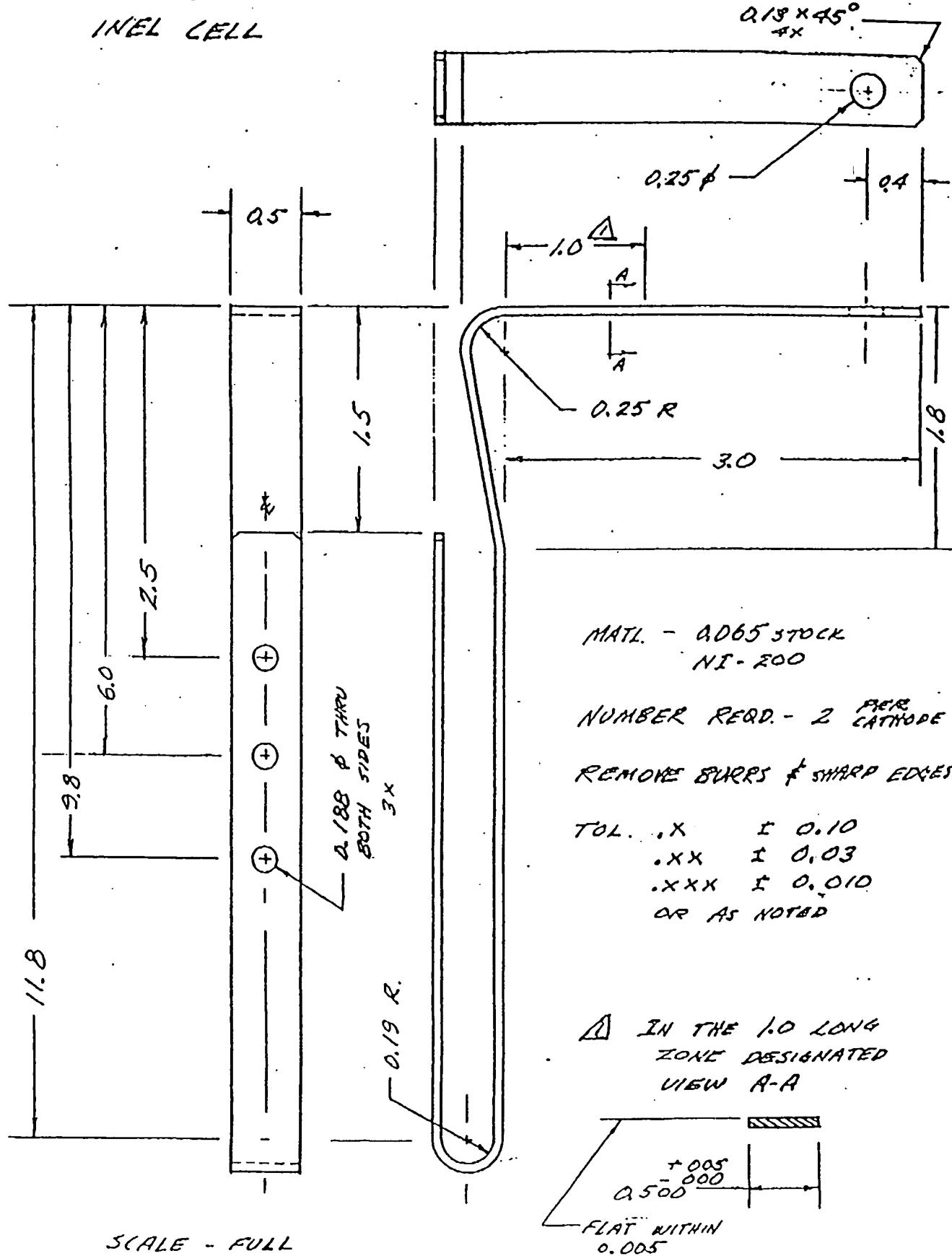
MATL. - 0.065 STOCK
NI - 200

NUMBER REQD. - 2 PER CATHODE

REMOVE BURRS & SHARP EDGES

TOL. .X   ± 0.10
.XX   ± 0.03
.XXX   ± 0.010
OR AS NOTED

IN THE 1.0 LONG
ZONE DESIGNATED
VIEW A-A

+.005
-.000
0.500

FLAT WITHIN
0.005

CATHODE C-1

INEL CELL

4.88" REF.

4.13"

NI-200
CATHODE
STRAP —
TWO AT
180°

WINDING
NI-200
WIRE
0.010 DIAM
3.33 LB
0.2 SOLID WRAP

10.0"

NUMBER REQD. — ONE PER CELL

10-19-92
10-21-92
12-7-93